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Additives for water mist fire suppression systems

A review

John A. Hiltz

Defence R&D Canada – Atlantic

Technical Memorandum
DRDC Atlantic TM 2012-236
November 2012

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Principal Author

Original signed by John A. Hiltz

John A. Hiltz

Defence Scientist

Approved by

Original signed by Leon Cheng

Leon Cheng

Head Dockyard Laboratory Atlantic

Approved for release by

Original signed by Leon Cheng

Leon Cheng

Chair/Document Review Panel

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Abstract

The use of both fixed and portable water mist systems for fire suppression on naval vessels continues to increase. There are several reasons for this. Water mist produces no acid gases and therefore can be discharged in a space where persons are present. It consists of small water droplets (average mean diameter of 90% of the droplets less than 300µm) that rapidly reduce the temperature in a space. The effectiveness of water mist in cooling a space reduces the volume of water necessary to extinguish or suppress a fire. This lessens both the chance of flooding and costs associated with cleanup arising from water damage.

In this report the use and efficacy of additives in water mist systems is reviewed. In most instances, additives have been investigated to determine if they will improve the efficacy of a water mist fire suppression system. Additives that have been investigated include film forming additives for Class B fires (generally fluorinated surfactants), alkali metals salts, transition metal chlorides, sulphates, phosphates and organic compounds such as sucrose and urea. In other instances, the additives were required to depress of the freezing point of the water used in the suppression systems. These suppression systems were proposed for use in conditions where the system might be exposed to temperatures below the freezing point of pure water. The additives included compounds such as potassium acetate and propylene glycol. The subsequent testing studied the effect of the additives on the water mist systems efficacy in suppressing a fire. Where information is available, the toxicity and other concerns associated with the use of additives are discussed.

Résumé

L’utilisation de systèmes d’extinction d’incendie à brouillard d’eau fixe et portatif sur les navires militaires continue de croître pour plusieurs raisons. Le brouillard d’eau ne contient pas de gaz acides et, par conséquent, peut être projeté dans un espace où se trouvent des personnes. Un système à brouillard d’eau consiste à pulvériser des gouttelettes d’eau (dont 90 % des gouttelettes ont un diamètre moyen inférieur à 300 µm) qui réduisent rapidement la température d’un espace. Il refroidit efficacement une pièce, ce qui permet de réduire le volume d’eau nécessaire à l’extinction d’un incendie. Ainsi, on réduit les risques d’inondation et les coûts associés au nettoyage des dommages causés par l’eau.

Dans le présent rapport, on a évalué l’utilisation et l’efficacité des additifs dans les systèmes à brouillard d’eau. Dans la plupart des cas, on a étudié les additifs pour déterminer s’ils pourront améliorer l’efficacité d’un système d’extinction d’incendie à brouillard d’eau. Les additifs étudiés comprennent notamment les additifs à formation de films pour les incendies de classe B (généralement des agents de surface fluorés), des sels métalliques alcalins, des chlorures métalliques de transition, des sulfates, des phosphates et des composés organiques, comme le saccharose et l’urée. Dans d’autres cas, les additifs devaient abaisser le point de congélation de l’eau utilisée dans les systèmes d’extinction d’incendie. On a proposé l’utilisation de ces derniers dans les cas où le système d’extinction pourrait être exposé à des températures sous le point de congélation de l’eau pure. Les additifs comprenaient des composés comme l’acétate de potassium

et le propylèneglycol. Les essais subséquents visaient à étudier les effets des additifs sur l'efficacité des systèmes à brouillard d'eau d'éteindre un incendie. Lorsque l'information est disponible, on peut analyser la toxicité et d'autres préoccupations associées à l'utilisation d'additifs.

Executive summary

Additives for water mist fire suppression systems: A review

John A. Hiltz; DRDC Atlantic TM 2012-236; Defence R&D Canada – Atlantic; November 2012.

Introduction: Halons have been the fire suppressant of choice for use in both fixed total flooding and portable fire suppression systems on board naval vessels. However, Halons deplete ozone and have been banned by many countries for use in fire suppression systems on new build naval vessels. Water mist is one of the alternatives for replacement of Halons. There are several reasons for this. Water mist is environmentally friendly and non-toxic. Other gaseous fire suppression agents that do not deplete ozone produce significant concentrations of acid gases when exposed to the high temperatures characteristic of a fire. This poses a threat to any persons in a space when the suppression system is activated, may increase re-entry times for damage control teams, and may cause damage to materials and electronic components exposed to the acid fumes. Water mist produces no acid gases and therefore can be discharged in a space where persons are present. It consists of small water droplets (average mean diameter of 90% of the droplets less than 300μm) that rapidly reduce the temperature in a space. The effectiveness of water mist in cooling a space reduces the volume of water necessary to extinguish or suppress a fire. This lessens both the chance of flooding and costs associated with cleanup arising from water damage. There has been a considerable amount of research focussed on the use of additives in water mist systems to enhance fire suppression. This is reviewed in this memorandum.

Results: Additives evaluated for use in water mist/fine water spray systems are reviewed. Many of the additives do improve the efficacy of water mist. The film forming additives, AFFF and Forafac® WM, were found to improve the effectiveness of a water mist/fine water spray systems against obstructed fires and, because they promote the formation of foam films on the fuel surface, impart resistance to re-ignition of the fuel.

Alkali metal salts, such as NaCl, KCl and $KHCO_3$, also significantly improve the effectiveness of water mist. However, they promote corrosion of metals and as such any space in which an alkali salt/water solution was used to suppress a fire would have to be cleaned thoroughly once the fire was extinguished. Metal halides, including cobalt, zinc and manganese chlorides, also improve the performance of water mist fire suppression systems but less than the alkali metal salts. Both the alkali metal and the metal chlorides can produce acid gas (HCl) and this will have an effect on re-entry and clean-up procedures for the space after a fire. The improved performance of water mist containing these additives is due to radical scavenging by the chloride ions and radical quenching mechanisms by the metal ions.

Potassium acetate, added to lower the freezing point of the water used in the fire suppression system, also enhanced the fire suppression performance of a water mist system.

Significance: Water mist/fine water spray is replacing Halon for ship board fire suppression applications in new build Royal Canadian Navy ships. For instance, the Fire Protection Design Statement for the Joint Support Ship lists the use of water mist and fine water spray for a number of shipboard spaces. Additives that can enhance the performance of these systems without

significantly increasing costs or introducing hazards to the ships' crew and its components are of interest.

Future plans: This research is part of the Project Arrangement on New Technologies for Fire Suppression On Board Naval Craft (FiST) under the Canada/The Netherlands/Sweden Cooperative Science and Technology Memorandum of Understanding. This project includes large scale fire testing of water mist systems, evaluation of aerosol fire suppressants, and studies of how new fire suppression technologies will impact firefighting doctrine. The results of the tests, evaluations and studies will be available to those specifying fire suppression systems and technologies for upcoming Royal Canadian Navy shipbuilding projects.

Sommaire

Additives for water mist fire suppression systems: A review

John A. Hiltz; DRDC Atlantic TM 2012-236; R & D pour la défense Canada – Atlantique; novembre 2012.

Introduction : On utilisait les halons comme agents extincteurs dans les systèmes d'extinction d'incendie par saturation fixes et portatifs sur les navires militaires. Toutefois, puisque ces substances appauvrissent la couche d'ozone, bon nombre de pays ont interdit leur utilisation dans les systèmes d'extinction d'incendie sur les navires militaires nouvellement construits. Pour plusieurs raisons, les systèmes à brouillard d'eau constituent l'une des options de remplacement des systèmes avec halons. Ce type de système est écologique et non toxique. D'autres agents extincteurs gazeux qui n'appauvrissent pas la couche d'ozone libèrent des concentrations importantes de gaz acides lorsqu'ils sont exposés à des températures élevées générées par un incendie. Ces gaz présentent un risque pour les personnes qui se trouvent à l'endroit où le système d'extinction a été activé; ils peuvent retarder l'entrée des équipes d'intervention, et causer des dommages au matériel et aux composants électroniques exposés aux vapeurs acides. Le brouillard d'eau ne contient pas de gaz acides et, par conséquent, peut être projeté dans un espace où se trouvent des personnes. Un système à brouillard d'eau consiste à pulvériser des gouttelettes d'eau (dont 90 % des gouttelettes ont un diamètre moyen inférieur à 300 µm) qui réduisent rapidement la température d'un espace. Il refroidit efficacement une pièce, ce qui permet de réduire le volume d'eau nécessaire à l'extinction d'un incendie. Ainsi, on réduit les risques d'inondation et les coûts associés au nettoyage des dommages causés par l'eau. On a effectué un nombre considérable d'études sur l'utilisation d'additifs dans les systèmes à brouillard d'eau qui permettraient d'améliorer l'extinction d'un incendie. Il en sera question dans le présent document.

Résultats : On a examiné les additifs évalués pour les utiliser dans les systèmes d'extinction à brouillard d'eau et à eau pulvérisée. Beaucoup d'additifs améliorent l'efficacité des systèmes à brouillard d'eau. Les additifs à formation de film, la mousse à formation de film flottant et les additifs Forafac® WM, augmentent l'efficacité des systèmes d'extinction à brouillard d'eau et à eau pulvérisée pour les incendies difficiles d'accès et, parce qu'ils forment une pellicule de mousse sur la surface de la matière combustible, ils réduisent les risques que celle-ci se rallume.

Les sels de métaux alcalins, comme le NaCl, le KCl et le $KHCO_3$, améliorent également l'efficacité des systèmes à brouillard d'eau. Toutefois, ils favorisent la corrosion des métaux; par conséquent, tout espace dans lequel une solution d'eau et de sel alcalin a servi à éteindre un incendie devra être méticuleusement nettoyé une fois l'incendie éteint. Les halogénures métalliques, y compris le cobalt, le zinc et les chlorures de manganèse, contribuent aussi à améliorer la performance des systèmes d'extinction d'incendie à brouillard d'eau, mais moins que les sels de métaux alcalins. Les métaux alcalins et les chlorures métalliques peuvent produire des gaz acides (HCl) qui peuvent retarder les procédures d'intervention et de nettoyage de l'espace après un incendie. La performance améliorée des systèmes à brouillard d'eau contenant ces additifs est attribuable au piégeage des radicaux à l'aide d'ions chlorure et aux mécanismes de désactivation des radicaux au moyen d'ions métalliques.

L'acétate de potassium, ajouté pour abaisser le point de congélation de l'eau utilisée dans le système d'extinction d'incendie, augmente également la capacité d'extinction d'un brouillard d'eau.

Importance : Le brouillard d'eau et la pulvérisation fine d'eau remplacent les halons dans les systèmes d'extinction des incendies à bord des navires nouvellement construits de la Marine royale canadienne. Par exemple, l'énoncé de la conception des systèmes de protection contre les incendies pour le navire de soutien interarmées énumère les espaces à bord d'un navire qui contiennent un système à brouillard d'eau et à pulvérisation fine d'eau. On s'intéresse aux additifs qui peuvent améliorer la performance de ces systèmes sans pour autant augmenter considérablement les coûts ou présenter des risques pour l'équipage et les composants des navires.

Plans futurs : La présente recherche fait partie de l'entente de projet sur les nouvelles technologies d'extinction des incendies à bord d'embarcations navales (projet FiST) relevant du protocole d'entente (PE) sur la coopération en science et en technologie conclu entre le Canada, les Pays-Bas et la Suède. Ce projet comprend des essais à grande échelle des systèmes à brouillard d'eau, l'évaluation d'agents extincteurs en aérosol et des études sur la façon dont les nouvelles technologies d'extinction des incendies influent sur la doctrine de lutte contre les incendies. Les résultats de ces essais, évaluations et études seront divulgués aux personnes précisant les technologies et les systèmes d'extinction des incendies pour les projets à venir de construction navale de la Marine royale canadienne.

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1 Introduction

Water mist systems are effective fire suppression systems for several reasons. Water has a high heat capacity (4.2 J/g-K) and high latent heat of vapourization (2.4 kJ/g) and therefore will absorb a large quantity of heat from the fire. Water also expands approximately 1700 times in the phase transition from the liquid to the gaseous state. This results in dilution of oxygen and combustible vapours in the vicinity of the fire. The steam also reduces the radiative heat transfer to the combustible materials' surface. This slows the release of thermal degradation products from solids or the volatilization of flammable vapours from liquids that are required for the combustion process.

In water mist fire suppression systems, pressure is used to produce smaller droplets than are produced by sprinkler systems. Water mist systems are traditionally categorised in three groups, based on the operating pressure, low pressure (up to 12.5 bar), medium pressure (between 12.5 bar and 35 bar) and high pressure (above 35 bar). By definition, 99% of the water droplets produced must be smaller than 1 mm in diameter in a water mist system. Smaller droplets have a greater surface area than larger droplets per unit mass. This enhances the evaporation rate of the water droplets and results in more rapid cooling of a space and subsequent lowering of both the oxygen and fuel vapour concentrations in the space. Thus the fire is suppressed or extinguished more rapidly.

Another advantage of water mist is that the volume of water required for fire extinguishment or suppression is reduced from that of traditional sprinkler systems or fire hoses. This results in reduced water damage and flooding.

Over the past 25 years, a number of studies have been carried out to determine if additives could be used to improve the performance of water mist fire suppression systems. The objectives of these studies have varied. In some instances the additives were used to lower the freezing point of water so that the system could be used at lower temperatures, in others the additives were investigated to determine if they would improve the systems performance against fires that were difficult to extinguish or to decrease the time to extinguishment of the fire.

Canada, The Netherlands and Sweden are involved in a Project Arrangement entitled "New Technologies for Fire Suppression On Board Naval Craft (FiST)" under the Canada/Netherlands/Sweden Cooperative Science and Technology Memorandum of Understanding. One of the collaborative activities under this Project Arrangement is a review of the use of additives to improve the performance of water mist fire suppression systems. This is the subject of this report.

2 Fire Suppression

The fire quadrangle is shown in Figure 1. Fuel, heat, oxygen (or an oxidant) and a sustaining chemical reaction are necessary for combustion to take place. To extinguish a fire requires that at least one of these four requisites be reduced to the point where combustion can no longer take place.

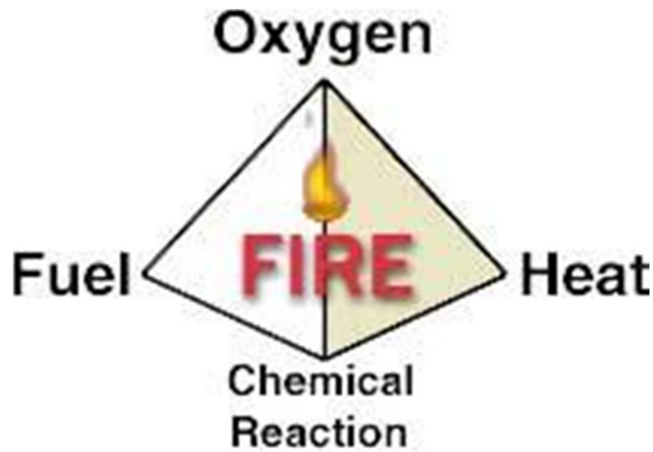

Figure 1: The requirements for combustion (fire), if any one of these is eliminated the fire will be extinguished.

Water acts to suppress fire by removing heat and reducing the concentration of oxygen and fuel available for the combustion reaction. Water with aqueous film forming foam (AFFF) produces a foam that blankets a burning liquid. In addition to the cooling, this barrier prevents the liquid from being volatolized and oxygen from reaching the fuel. These are physical mechanisms. In contrast to water mist, some gaseous agents, such as Halon 1301, suppress fires by interfering with (eliminating) the chemical reactions that drives the fire. This is a chemical mechanism.

$$RX \rightarrow R^{\bullet} + X^{\bullet}$$

X may be Br or Cl

$$X^{\bullet} + R'H \rightarrow R'^{\bullet} + HX$$

$$HX + H^{\bullet} \rightarrow H_2 + X^{\bullet}$$

$$HX + OH^{\bullet} \rightarrow H_2O + X^{\bullet}$$

Figure 2: Radical ($H^{\cdot}$, $OH^{\cdot}$) scavenging mechanisms of gaseous fire suppressants (RX) containing chlorine (Cl) and bromine (Br).

Metal oxides and hydroxides are effective flame suppressants that act via a chemical mechanism. For instance, iron and manganese oxides and hydroxides are involved in a catalytic radical recombination cycle that removes hydrogen radicals from a flame [1]. The reactions are shown in Figure 3.

In the following sections, the results of studies of the effectiveness of additives used in water mist systems are discussed. Their effectiveness is related to either physical or chemical mechanisms that lead to extinguishment or suppression of the combustion process. Additives may also affect the droplet vaporization and generation processes by reducing surface tension or by acting as a wetting agent. Changes in droplet size or the time that a water-based suppressant is in contact with a surface will change the rate and/or the amount of heat that the suppressant will remove from the combustion reaction and therefore the efficacy of the suppressant.

$$FeOH + H^{\bullet} \leftrightarrow FeO + H_2$$
$$FeO + H_2O \leftrightarrow Fe(OH)_2$$
$$Fe(OH)_2 + H^{\bullet} \leftrightarrow FeOH + H_2O$$
$$\text{Net reaction: } H^{\bullet} + H^{\bullet} \leftrightarrow H_2$$

Figure 3: Catalytic hydrogen radical recombination cycle involving iron oxides and hydroxide.

3 Water Mist Additives

3.1 Aqueous film forming foams (AFFF)

A series of low pressure water mist/fine water spray fire suppression tests involving the use of aqueous film forming foams (AFFF) and wetting agents were carried out by the Ministry of Defence in the United Kingdom [2-5]. Five additives were evaluated: additive 1 and 2 were AFFF formulations (MIL Specification MIL-F-24385 and Def Stan 42/40-1 respectively) that are in use in a variety of military applications, additive 3 was a film forming fluoro protein (FFFP) foam, and additive 4 (Fire Stopper) and additive 5 (Fuel Buster) were wetting agents. Company literature indicated that Fire Stopper was formulated to be more environmentally friendly than existing additives and that the enhanced performance of Fuel Buster was achieved by locking up fuel in small droplets surrounded by the agent. All additives were used at the manufacturers recommended concentration.

Four of the additives were tested using a sprinkler nozzle (MV34) and a fine water spray (FWS) nozzle (GW K-15) [2]. The mean diameter of the water droplets produced by the GW K-15 nozzle was between 200 and 300 µm. The FWS nozzle has a K factor of 15 and used approximately one quarter of the water of the MV34 sprinkler. The results of the tests are shown in Table 1. The use of additives improved the performance of the MV34 sprinkler system over that found for water alone with respect to both extinguishment time and volume of water used except for Fuel Buster. In the tests using the Fuel Buster additive the fire was not extinguished. The additives (except for Fuel Buster) also improved the performance of the water spray system with the GW K-15 nozzles. Both the time to extinction and the volume of water to extinguish the fires were reduced compared to the sprinkler system.

The results of the burnback tests for the water, either seawater or freshwater, with additives are shown in Table 2. Burnback is described in MIL-F-24385 and for a film forming foam to be certified to this specification it must have a burnback time greater than 360 seconds. The FFFP additive gave the best burnback performance (longest burnback time) in sea water and the second best time in fresh water. The burnback time of the Fuel Buster additive in water was the longest but it took significantly longer to extinguish the fire prior to the burnback test.

Observations made during the testing suggested that the additives might be affecting the mean diameter of the water droplets being produced by the FWS nozzle. Seawater with AFFF was selected for use in subsequent tests; seawater because it could be supplied by seawater (fire main) systems on Naval vessels and AFFF (MS) because it was used on Naval vessels.

The results of a series of fire tests using AFFF (MS) and four FWS nozzles (see Table 3) are shown in Table 4. The results clearly show the advantage of using additives in the FWS system for Class B (liquid fuel) fires. Significant reductions in extinguishment times compared to saltwater alone were observed. For instance, when using the GW K-15 nozzles the extinguishment time of a dieso (diesel fuel) fire decreased from 175 seconds to 8 seconds when the additive was used and an Avtur (aviation turbine fuel) fire that was not extinguished with seawater was extinguished in 10 seconds with the additive. The use of additive was far less effective in reducing extinguishment times for Class A fires. For instance, extinguishment times for the wood crib fire increased when the additive was used for two of the nozzles tested. It was noted in the report that this should not be unexpected as the additive (AFFF (MS)) was developed to improve performance against Class B fires.

Table 1: Summary of results of fire suppression testing using sprinkler and water spray nozzles to deliver water containing AFFF MIL Spec (MS), FFFP, Fire Stopper (FS) and Fuel Buster (FB) additives (from reference 2).

System	Additive Type	Delivery Pressure (bar)	Water Used (L)	Ext. Time (sec)
Sprinkler (MW34)	None	7.0	419	75
	AFFF (MS)	7.0	201	36
	AFFF (MS)	3.5	245	61
	Add (FFFP)	3.5	205	51
	Add (FS)	7.0	120	30
	Add (FB)	3.5	Not extinguished	Not extinguished
FWS (GW K-15)	None	7.0	167	63
	AFFF (MS)	7.0	40	15
	AFFF (MS)	3.5	15	8
	FFFP	3.5	15	8
	Add (FS)	7.0	26	10

The additive also reduced the volume of water necessary to extinguish the Class B fires substantially. The results are shown in Table 5.

The droplet characteristics of the GW Low Flow K15-C nozzle with a K factor of 15 were analysed using laser phase Doppler anemometry [3]. The results indicated that the nozzle produced a range of droplet sizes from 100 to 400 microns with a Dv of 322 microns. The larger droplets delivered additive to the fire while the smaller droplets maintained a floating water mist fraction. The nominal flow rate of the nozzle (39 L/min at 7 bar), although greater than that for a water mist nozzle, still resulted in reduced water consumption compared to existing RN sprinklers. Subsequent testing indicated that the water mist quality improved as the AFFF concentration was reduced. For instance, reducing the water/AFFF ratio from 94/6 to 99.5/0.5 (for the 6% AFFF concentrate) resulted in improved fire suppression performance. However, the burnback protection was decreased somewhat. The optimum mix of fire suppression and burnback properties were observed for a 1 vol% solution of AFFF (6% concentrate) in water.

The chemical and physical effects of AFFF in the fine water spray system were also studied [4]. There was no evidence that AFFF aided in suppressing fires through a chemical mechanism. The improved performance was attributed to the larger water droplets and increase in droplet mean diameters produced with the additive. It was postulated that the larger droplets penetrate the fire and move to the flame region and fuel surface of unobstructed fires more effectively.

Table 2: Burnback results for salt and fresh water solutions of AFFF MIL Spec (MS), AFFF Defence Standard (DS), FFFP, Fire Stopper (FS) and Fuel Buster (FB) additives delivered through a water spray nozzle (from reference 2).

Additive Type	Water Source	Burnback (min:sec)
AFFF (MS)	Sea	6:00
AFFF (DS)	Sea	11:00
Add (FFFP)	Sea	12:00
Add (FS)	Sea	4:00
Add (FB)	Sea	Not extinguished
None	Fresh	6:30
AFFF (MS)	Fresh	5:00
AFFF (MS)	Fresh	14:47
FFFP	Fresh	2:37
Add (FS)	Fresh	30:00+

Table 3: Fine water spray nozzle parameters (from reference 2).

System	Bore (mm)	Output @ 3.5 bar (L/min)	Output @ 7.0 bar (L/min)	K-Factor	Rec. Delivery Pressure (bar)	Max. Nozzle Spacing (m)	Max. Spacing from Wall (m)
GWK-15	5.0	28.0	40.0	15	6.0-16.0	3.5	1.75
GWK-20	10.0	37.4	52.0	20	6.0-16.0	1.5	1.75
MV10	5.1	30.0	42.0	15.9	1.4-7.0	Not Available	Not Available
CL7	7 x 1.0	20.0	41.0	15.5	0.7-7.0	Not Available	Not Available

Table 4: Fire extinguishment times for FWS nozzles using seawater and saltwater and AFFF (MS) on a number of Class A and Class B fires (from reference 2).

System	Additive Used	Extinguishing Time (sec)					
		Dieso	Avtur	Heptane	Wood Crib	Cable	Dieso-soaked Insulation
GW K-15	No AFFF (MS)	175	Not Extin.	Not Extin.	22	226	620
		8	10	18	13	64	154
GW K-20	No AFFF (MS)	62	Not Extin.	Not Extin.	16	61	754
		7	8	14	38	10	83
MV10	No AFFF (MS)	95	450	228	41	24	Not Extin.
		14	21	30	62	165	247
CL7	No AFFF (MS)	644	740	Not Extin.	106	129	836
		15	6	11	14	134	242

Table 5: Volumes of water used to extinguish fires with seawater and seawater with AFFF (MS) (from reference 2).

System	Additive Used	Water used to Extinguish (L)					
		Dieso	Avtur	Heptane	Wood Crib	Cable	Dieso-soaked Insulation
GW K-15	No AFFF (MS)	463.8	Not Extin.	Not Extin.	58.3	598.9	1643.0
		21.2	26.5	47.7	34.5	169.6	408.1
GW K-20	No AFFF (MS)	219.1	Not Extin.	Not Extin.	56.5	215.5	2664.0
		24.7	28.3	49.5	134.3	459.3	293.3
MV10	No AFFF (MS)	266.0	126.0	638.4	114.8	448.0	Not Extin.
		39.2	58.8	74.0	171.0	462.0	691.6
CL7	No AFFF (MS)	1760.3	2022.7	Not Extin.	289.7	352.6	2285.0
		41.0	16.4	30.1	38.3	366.3	661.5

3.2 Quad-Ex

The United States Naval Research Laboratory carried out water mist fire suppression tests using Quad-Ex as a water additive in the 1990s. Quad-Ex (LaRoche Company) is primarily a mixture of potassium carbonate (K_2CO_3) and water and can be premixed with or injected into the water used in the mist system. The first series of tests evaluated the additive effectiveness in suppressing fires in a 3.0 m x 3.0 m x 2.4 m box against eight small (1 kW) heptanes pan fires [6]. The fires were located in each corner of the test space, in the center of the space under an obstruction, and on a ladder in one corner 0.6 m, 1.2 m, and 1.8 m above the floor. The test space and location of the fires are shown in Figure 3.

The water mist system consisted of a single modified nozzle (Model 1-7N-2) located in the center of the overhead of the room and was operated at 10 MPa (1500 psi) at a flow rate of 5.3 L/min and an application rate of 0.57 L/min/m^2. The fires were allowed to burn for one minute prior to the activation of the system. The results of the tests are shown in Table 6. The effectiveness of the water mist system improved as the volume percent of Quad-Ex in the water was increased up to 50%. However, even at 50% Quad-E the ladder fires 1.2 m and 1.8 m above the floor were not extinguished. No attempt was made to evaluate the toxicity or corrosiveness of the additive.

A series of large scale tests of the effectiveness of Quad-Ex were also carried out in a machinery space mock-up [7]. The test space was approximately 9.1 m x 9.1 m x 4.6 m and had a vent opening 3.0 m x 1.5 m located low in the center of one bulkhead. A diesel engine mock-up was positioned in the center of the space. The space was instrumented to measure both the thermal conditions in the space as well as the concentrations of gases in the space including carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2).

The water mist system used in this evaluation (Securiplex System 2000) was a twin fluid system which requires an atomizing fluid (air) to shear the water at the nozzle into small droplets. The system operated at approximately 5.5 bar (80 psi) for both fluids and produced medium size droplets (~200 microns). Thirty-six Securiplex nozzles were installed in the overhead of the space with a nominal spacing of 1.5m. Each nozzle delivered fluid at a rate 5 L/min producing a total flow of 180 L/min into the space.

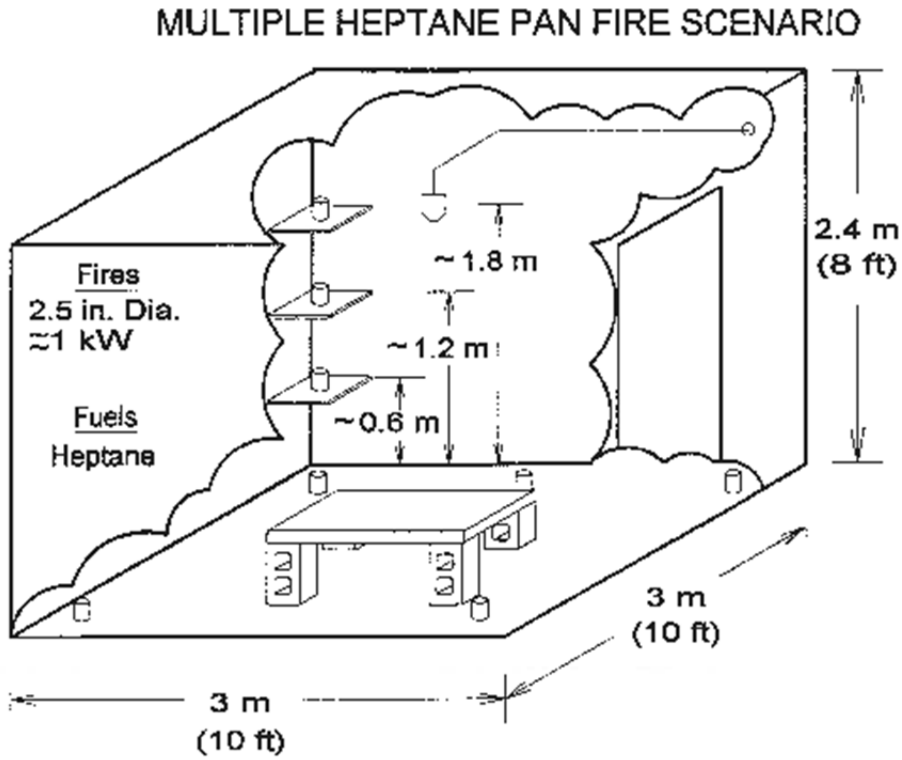

Figure 4: Set up for the multiple heptane pan fire suppression tests.

The suppression/extinguishment of the additives was evaluated against a 6.0 MW heptane spray fire (one minute preburn time) located on top of the diesel engine mock-up positioned in the center of the space. Tests were conducted using water only and water containing either 12% or 25% Quad-Ex by volume. The results are shown in Table 7.

Table 6: Results of small scale fire suppression tests using Quad-Ex in a water mist system [6].

Mixture Percent QUAD-EX (by volume)	Test No.	Application Rate (L/min/m^2)	Results						
			Ladder (m)			Floor/Corners			
			0.6	1.2	1.8	NW	NE	SW	SE
0	7	0.57	NE	NE	NE	NE	E	NE	NE
5	3,4	0.57	NE	NE	NE	E	E	NE	NE
10	1	0.57	NE	NE	NE	E	E	NE	NE
20	2	0.57	NE	NE	NE	E	E	E	E
30	5	0.57	NE	NE	NE	E	E	E	E
40	6	0.57	NE	NE	NE	E	E	E	E
50	8	0.57	E	NE	NE	E	E	E	E

Table 7: Results of large scale (engine room mock-up) fire suppression tests using Quad-Ex in a water mist system [7].

Fire Size (MW)	Fire Extinguishment Mixture Water/Quad-Ex (volume %)	Extinguishment Time (s)
6	100/0	Not extinguished (a)
6	75/25	30
6	88/12	20
6	88/12	20

(a) – two minute water mist supply

Although the additive improved the effectiveness of the suppression system, it was concluded that an additive would only be considered for a water mist system if an optimized water mist system (and the authors stated that the system used in this test series was not optimized) could not extinguish fires in a large space.

3.3 Multi-Component (MC) Additive

MC Additive [8] is an additive proposed for use in water mist systems. Its components and their concentrations are listed in Table 8. MC Additive is reported to be both non-corrosive and non-toxic.

Experiments were conducted in a 3.0 m x 3.0 m x 3.0 m glass-walled enclosure. Six thermocouples were placed directly above the fire with a gap of 0.02 m between adjacent thermocouples. The water mist nozzle was located 2.5 m directly above the fire. A 0.33 m diameter pan with a lip height of 0.05 m was used for the ethanol and diesel pool fire tests. Tests were also conducted using 0.4 m x 0.4 m x 0.28 m high wood cribs which were made from 0.04 m x 0.04 m pine sticks with 10 wt% water content. A 0.25m diameter pan with 0.15 kg ethanol fuel was placed under the crib. The distance between the pan and the wood crib was 0.25 m. The wood crib was ignited by the ethanol. The burning ethanol was removed after 150 s and the wood crib allowed to continue to burn for 30 s before activation of the water mist system. This allowed the fire to reach a fully developed stage. For the ethanol and diesel pool fire, a 30 s of pre-burn was allowed to reach steady burning conditions.

Table 8: Composition of MC Additive.

Component	**Purpose**	**Weight percent (wt %)**
$(C_2F_5)_2(CF_3)C(CF_3)C{=}C(CF_3)OC_6H_4SO_3Na$	surfactant	15.4
$C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$	Viscosity modifier	7.7
Carbamide (Urea)	Heat absorption/inert gas production	20.5
N,N-dimethylformamide	Solvent/freezing point depression	51.2
sodium acetate	Source of active radicals	5.2

A single fluid nozzle, that is, a nozzle that relied on the hydraulic pressure to force water through small diameter orifices and produce the mist, was used. The results of the tests on diesel fuel, ethanol and wood crib fires are shown in Table 9. The time to extinguishment of the diesel fuel fires decreased as the concentration of the additive was increased to 0.2 wt. % and then increased as the concentration was increased to 0.3 wt %. Extinguishment times were longer for the ethanol fires than the diesel fuel fires but the time to extinguishment decreased, as was observed for the diesel fuel fires, as the concentration of the additive was increased to 0.2 wt %. Above 0.2 wt % additive, the extinguishment times began to increase again. The extinguishment times for the wood crib fires decreased up to an additive concentration of 0.8 wt % and then increased as the concentration of additive was increased further.

The enhanced performance of the water mist system using the additive was attributed to both physical and chemical extinguishing mechanisms of the constituents of the additive. In reference [8], the authors indicate that the additive does not cause corrosion of metals. They also claim that the constituents of MC Additive are non-toxic.

Table 9: .Weight percent (wt %) MC Additive in water and corresponding extinguishment times for a) diesel fuel, b) ethanol and c) wood crib fires.

a) Diesel fuel

Additives, wt%	0	0.1	0.15	0.2	0.25	0.3
t/s	10.0	6.00	3.60	1.75	3.10	3.75

b) Ethanol

Additives, wt%	0	0.05	0.10	0.15	0.20	0.30	0.40	0.50	0.60
t/s	27.0	8.00	7.43	6.50	4.80	5.84	6.45	6.76	9.00

c) Wood crib

Additives, wt%	0	0.2	0.4	0.6	0.8	1.0
t/s	32	20	12	7.6	5.7	6.2

3.4 Potassium Acetate

In applications where the feed water for a water based fire suppression system can reach temperatures below 0°C, the use of additives to depress the freezing point have been studied. These include glycols, such as propylene glycol, and metal salts such as potassium acetate [9]. Both were found to produce solutions with freezing point depressions required for the water mist system application. However, propylene glycol will combust and this negates the gas phase cooling effect of the water mist. On a mass basis, propylene glycol/water solutions are predicted to be less effective than water in extinguishing a fire.

The fire suppression effectiveness of potassium acetate/water solutions were found be greater than that of water [10]. The testing was carried out in a mist adapted cup burner apparatus. The apparatus is shown in Figure 4 and its operation is described in Reference 9.

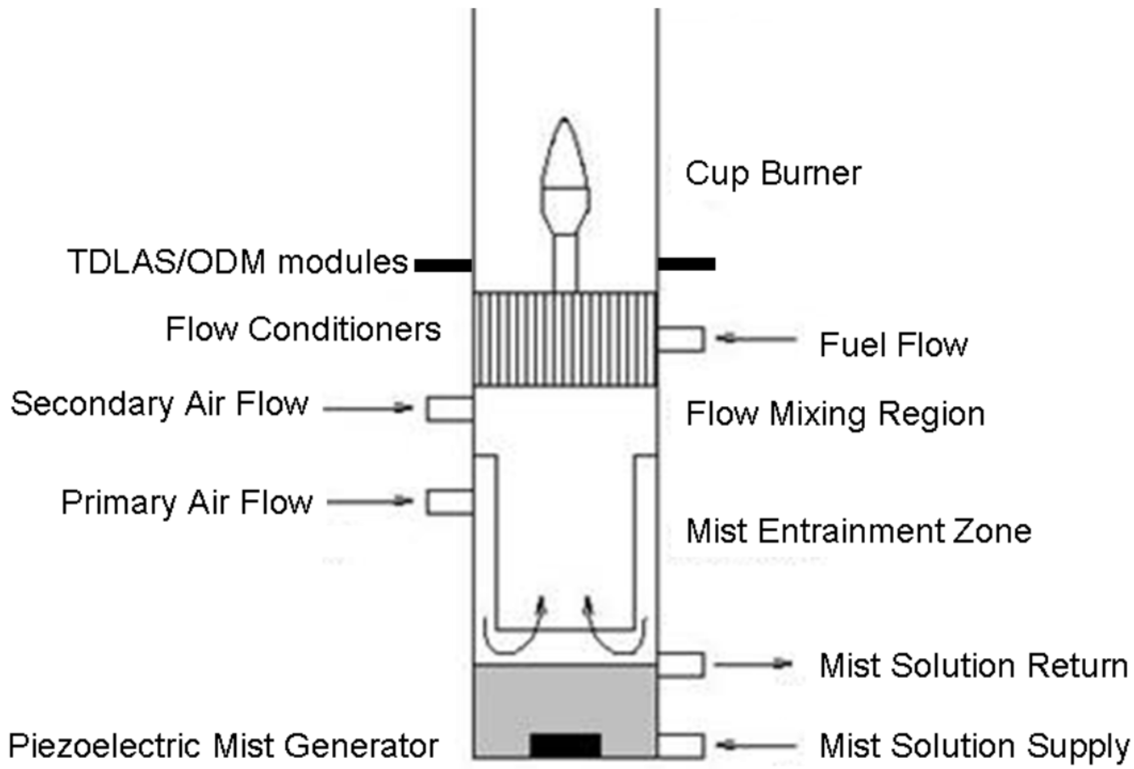

Figure 5: Schematic of the mist adapted cup burner apparatus used to evaluate the suppression effectiveness of potassium acetate/water solutions. TDLAS/ODM is a tunable diode laser absorption spectroscopy/optical density meter used to measure the mass of liquid water droplets in the oxidizer stream [10].

The suppression results for water and water solutions containing 3.wt % and 6.25 wt % potassium acetate are shown in Figure 5. The stable flame region was dramatically reduced for mists of either a 3.2 wt % or 6.25 wt % aqueous potassium acetate solution. The 3.2 wt % mist was approximately 2.3 times as effective at flame extinction and the 6.25 wt % mist was approximately 2.8 times more effective compared to pure water mist. The effectiveness of the added potassium acetate was not observed to increase in a linear manner with concentration. This was attributed to two limiting suppression phenomena: a thermodynamic limitation of the concentration of the catalytic species in the flame environment responsible for suppression and a limitation of any catalytic suppression agent to only lower the key flame propagation radicals to their equilibrium values. A reduction in flame temperature is also required for extinction and this is met by the cooling provided by the water mist.

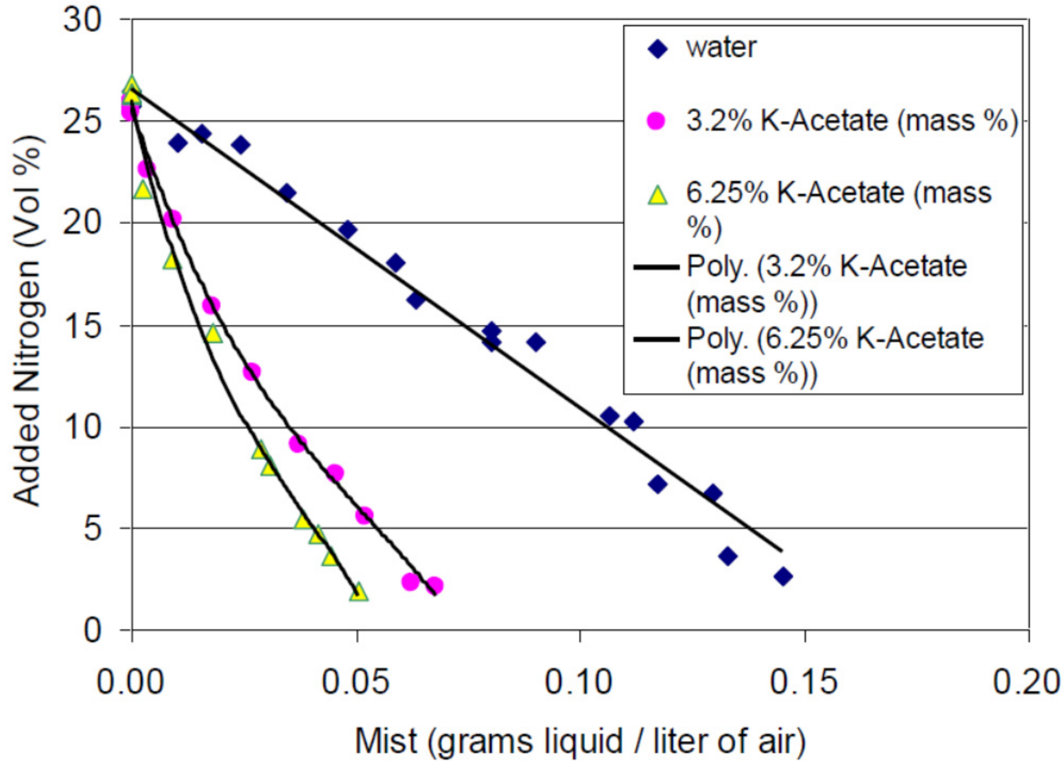

Figure 6: Plot of the results of the mist adapted cup burner apparatus fire extinguishment tests for water, 3.2 wt % potassium acetate, and 6.25 wt % potassium acetate. Flames are stable for the nitrogen/mist combinations below the lines [10]. Poly refers to the polynomial fit of the data for the 3.2 wt % and 6.25 wt % potassium acetate solutions extinguishment experiments.

3.5 Forafac® WM

Forafac® WM is a fluorinated surfactant supplied by Dupont. It has been investigated as an additive for water mist systems [11]. Dupont indicates there are several advantages resulting from the use of this additive with water in a water mist system. These include improved spreading of the additive water solution on metallic surfaces and higher cooling efficiency of the solution compared to water alone. The film forming properties of the additive water solution also result in reduced fire extinction times and improved protection against re-ignition.

The efficacy of 0.5 vol% and 2.0 vol% solutions of Forafac® WM in water in extinguishing fires (210 kW heptane pan fires) has been evaluated against pure water in a well-ventilated 3.6 m x 2.0 m x 1.2 m (9.1 m^3 volume) enclosure. The pan had a diameter of 0.53 m and a surface area of 0.22 m^2 and was located away from the center of the test compartment. The water mist/ Forafac® WM solution was delivered at a rate of 22.7 L/min through a single nozzle (AM4) located in the center of the compartment near the ceiling. The results of the fire extinguishment tests are shown in Table 10. The fire was not extinguished using water mist without the additive. However, water mist containing Forafac® WM extinguished the fire. The time to extinguish the fires decreased when the concentration of the additive was increased from 0.5 vol% to 2.0 vol%.

Table 10: Heptane pan fire extinguishment times for water mist, and water mist with 0.5 vol% and 2.0 vol% Forafac® WM. NA refers to the fact that the fire was not extinguished by the water mist. It went out at the times noted because all the heptanes in the fuel pan had been combusted.

Concentration of Active Matter	Pure Water	0.5% Forafac	2% Forafac
Test 1 Extinction Time (s)	NA* (460)	196	70
Test 2 Extinction Time (s)	NA* (429)	231	110
Average Extinction Time (s)	NA* (435)	214	90

The burnback time for the fuel was greater than 9 minutes when the additive was used in the water mist system. This results from the formation of a layer of foam on the fuel surface. Without the additive, the fuel could be re-ignited immediately.

Forafac® WM in water was also tested in a larger enclosure (8.02 m x 4.17 m x 1.70 m or 56 m^3) on kerosene and heptanes fires. The square fuel pan (0.5 m x 0.5 m) was centered under a table like obstruction (2.1 m x 1.1 m x 0.8 m) that had two sides that could be removed. Two water mist nozzles (Life Mist Yulian) were used to suppress the fires. Yulian nozzles use compressed gas (air in this study) to form water mist. The results of the tests are shown in Table 11.

Table 11: Results of fire extinguishment tests on kerosene or heptanes pan fires using water mist and water mist with 2 vol% Forafac® WM.

Test	Forafac® WM (%)	Fuel	Obstruction	Side Panels	Time to Extinguishment (s)
1	0	Kerosene	Table	Yes	556
2	2	Kerosene	Table	Yes	282
3	2	Kerosene	Table	Yes	371
4	2	Kerosene	Table	No	104
5	2	Heptane	No	No	143
6	0	Heptane	No	No	322

The time to extinguishment decreased significantly for water containing 2 vol% Forafac® WM. This was observed for both kerosene and heptanes fires. It is interesting to note the difference in extinguishment times for tests 2 and 3 (282 s versus 371 s) that were carried out under the same test conditions.

Testing of the toxicity of water mist containing Forafac® WM was also carried out using the protocol found in "Inhalation Median Lethal Concentration (LC50) Study in Rats". In the tests, 10 male and 10 female rats were exposed to a water mist containing 2 vol% Forafac® WM (5.9 mg of solution/liter of air) for 4 hours. The histopathology of the respiratory tract of half of the population was analyzed 24 hours after the exposure. The other half of the population was weighed and observed for clinical signs of toxicity during a 14-day recovery period.

All rats survived the exposure and the subsequent 1 or 14 day recovery periods. Some male and female rats exhibited slight body weight losses the day after the exposure. This was followed by normal weight gain for the remainder of the recovery period. Ocular discharges were observed in some rats following the exposure. No other clinical signs of toxicity were observed throughout the recovery period. A gross pathological examination revealed no evidence of organ-specific toxicity for rats sacrificed approximately 24 hours after the exposure or at the end of the 14 day recovery period.

The corrosivity of water containing 2 vol% Forafac® WM was compared to that of water. Aluminum, cast iron, steel, stainless steel, copper, and a titanium alloy (TA6V) coupons were immersed in the two fluids and it was found that the additive did not alter the amount of corrosion suffered by the coupons.

3.6 Chlorides, carbonates, phosphates, sulfates, urea and sucrose

A series of chemical additives, including sodium chloride (NaCl), potassium chloride (KCl), cobalt chloride ($CoCl_2$), zinc chloride ($ZnCl_2$), manganese chloride ($MnCl_2$), potassium bicarbonate ($KHCO_3$), ammonium hydrogen phosphate ($(NH_3)_2HPO_4$), iron sulfate ($FeSO4_{\cdot}7H2O$, urea and sucrose have been evaluated as additives for water mist systems [12].

The effectiveness of the additives was studied using the apparatus shown in Figure 6. A 50 mm diameter heptane pool fire was contained in the compartment that was constructed of 10 mm thick poly(methylmethacrylate). The water mist was estimated to have an initial velocity of 4 m/s and a mean droplet diameter of 27 µm. A 1 mm aperture nebulizer with an uptake of 24 mL/min, under 2 bar pressure was used to produce the water mist. The spray cone angle was estimated to be 60^o. A wooden obstruction was positioned 10 cm from the central axis of the nebulizer to prevent the momentum of the mist flow from directly extinguishing the flame. This allowed the mist to act as a flooding agent.

To prevent extinction of the fire through oxygen depletion, the compartment was supplied with a continuous flow of air. Two exhaust holes in the roof of the compartment were left open throughout the experiment. When no water mist was introduced to the compartment, the heptane fire burned for at least twenty minutes. The fire went out once the fuel had been consumed. In the water mist additive tests, mist was introduced into the compartment and times to extinction of the fire were measured.

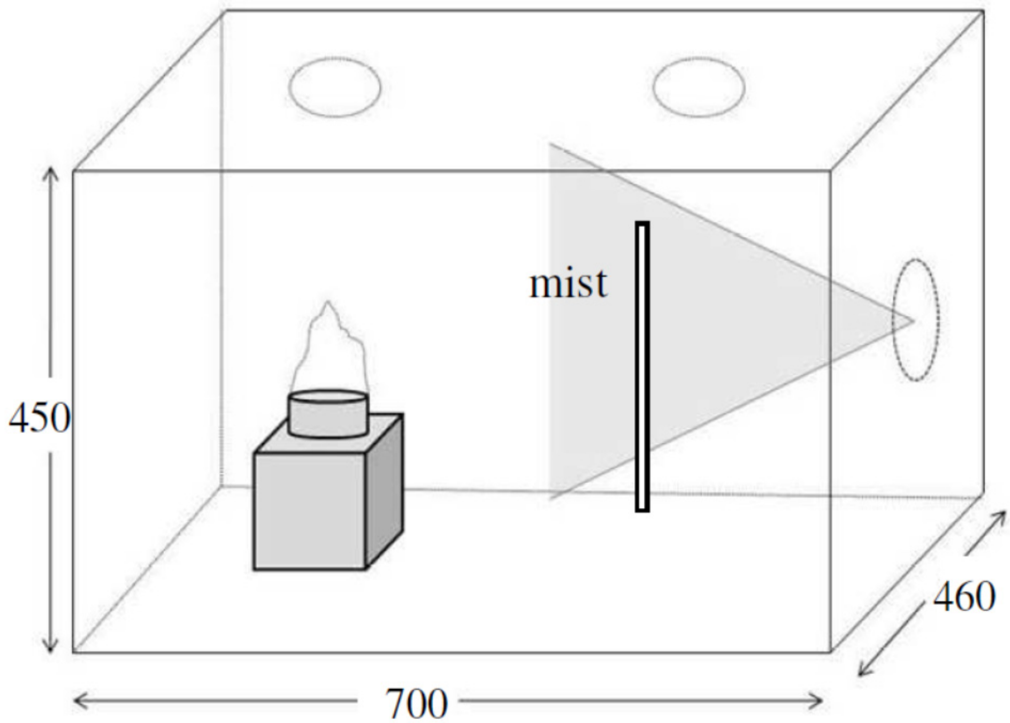

Figure 7: Test compartment used to evaluate water mist additives (Reference [12]).
All measurements are millimetres (mm).

The results of the tests are shown in Figure 7. Solutions containing 3 wt% alkali metal salts (NaCl, $KHCO_3$, or KCl) were found to be the most effective fire suppressants while solutions containing 3 wt% $FeSO_4 \cdot 7H_2O$, urea, or $(NH_3)_2HPO_4$ were less effective than water mist. Solutions containing cobalt, zinc and manganese chlorides and sucrose were all more effective fire suppressants than water but were less effective than the alkali metal salts. Copper chloride ($CuCl_2$) was also investigated in this study but the concentration of acid gas (HCl) produced by this additive was deemed to be unacceptable high.

The effectiveness of the alkali metal salts was attributed to the radical scavenging ability of the halide ions and the radical quenching properties of the alkali metal ions. Both disrupt the chemical reactions required for the propagation of the fire. The metal chlorides function in a similar manner. The chloride ions scavenge radicals and the metal ions quench radicals. The poor performance of the solutions containing urea or $(NH_3)_2HPO_4$ was attributed to their decomposition at higher temperatures to produce volatile products (ammonia, NH3) that sustained the flame. The poor performance of the FeSO4.7H2O solution was unexpected but the authors surmised that it might be due to the sulfate counter anion having an antagonistic effect on the flame.

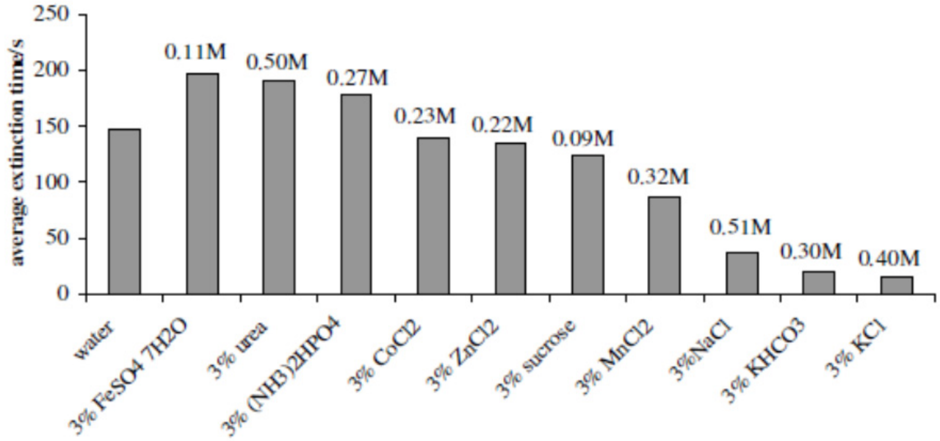

Figure 8: Extinguishments times for water mist solutions containing 3 wt% (weight/volume) of ten additives. The molarity of each of the additives is also shown.

The use of alkali metals halides solutions in fire suppression systems in shipboard spaces has a number of drawbacks. They produce acid gas (HCl) that is both toxic and corrosive. The salts themselves would promote corrosion and any space in which they were used would have to be thoroughly cleaned to prevent this.

4 Summary and Conclusions

There has been a considerable amount of research in the use of additives for water mist systems. The majority of this research has investigated how (or if) the additives enhance the effectiveness of water mist fire suppression. There was one example of the use of additives to decrease the freezing point of water. In that instance, the water mist system was to be used at temperatures below 0^oC.

The UK Ministry of Defence has carried out an extensive program that investigated the use of AFFF (MIL Specification MIL-F-24385 and Def Stan 42/40-1) and wetting agents to enhance the performance of a low pressure (7 bar) fine water spray fire suppression system. The results indicated that the time to extinguishment and burnback resistance of the water mist with AFFF (94/6) improved over that for water alone. The volume of water required for fire extinguishment decreased significantly when water with AFFF was used. It was also observed that when the water/AFFF (6% concentrate) ratio was reduced from 94/6 to 99.5/0.5 that the fire extinguishment times decreased. However, the burnback times also decreased. A 99/1 water/AFFF ratio was selected to optimize fire extinguishment and burnback properties.

Quad-Ex (primarily a mixture of K_2CO_3 in water) has been evaluated as a water mist additive in both high and low pressure systems. High pressure testing (~100 bar) was carried out in a 3.0 m x 3.0 m x 2.4 m box against eight small (1 kW) heptanes pan fires. Fire suppression times were found to decrease as the concentration of Quad-Ex was increased to 50 wt%. However, small fires located 1.2 m and above the floor of the compartment were not extinguished. In a larger compartment (9.1 m x 9.1 m x 4.6 m) and using a low pressure system (5.5 bar), 12 wt% and 24 wt% solutions of Quad-Ex extinguished a heptane spray in 20 and 30 seconds respectively. Without the additive the system did not extinguish the fire. No studies of this additive's toxicity were carried out. It was concluded that the use of additives, such as Quad-Ex, would only be considered if the optimized water mist system could not extinguish fires in the space it was protecting. It was noted that the water mist system used in the low pressure tests was not optimized.

The effectiveness of MC Additive as a water mist additive was evaluated on diesel and alcohol pool fires and wood crib fires in a 3.0 m x 3.0 m x 3.0 m compartment. Fire extinguishment times for the pool fires decreased as the concentration of additive was increased to 0.2 wt % and then began to increase again as the concentration of the additive was increased. For the wood crib fires, extinguishment times decreased as the concentration of additive was increased to 0.8 wt %. The enhanced performance of water mist systems using this additive have been attributed to both chemical and physical extinguishing mechanisms of the constituents of the additive.

Potassium acetate, added to lower the freezing point of water, was found to enhance the flame extinction of water mist in a cup burner apparatus. A 3.2 wt % potassium acetate in water was approximately 2.3 times as effective as water alone. The enhancement did not increase linearly with potassium acetate concentration. This was attributed to two phenomena, a thermodynamic limitation of the concentration of catalytic species in the vicinity of the flame and a limitation of the catalytic species to lower the flame propagation radicals to their equilibrium concentration. This additive has not been tested in a larger scale fire suppression test.

Forafac® WM is a fluorinated surfactant that has been evaluated as a water mist additive in 9.1 m^3 and 56 m^3 compartments using an AM4 and Yulian nozzles respectively. Testing indicated that water containing 2 vol% of this additive was more effective as a fire suppressant than water alone. This additive also imparted burnback resistance to the water mist and improved the ability of the system to extinguish obstructed fires. The authors of the report stated that the additive was non-toxic and testing indicated the additive did not increase corrosion of metals over that observed for water alone.

Small scale tests (0.70 m x 0.46 m x 0.45 m compartment) indicated that 3% solutions (mass/volume) of alkali metal salts (NaCl, KCl, and $KHCO_3$) in water significantly enhanced extinction times for heptane fires over water alone. Solutions containing 3% (mass/volume) cobalt, zinc and manganese chlorides and sucrose were all more effective fire suppressants than water too, but were less effective than the alkali metal salts. The effectiveness of the alkali metal salts was attributed to the radical scavenging ability of the halide ions and the radical quenching properties of the alkali metal ions. Both disrupt the chemical reactions required for the propagation of the fire.

These additives were not evaluated in large scale fire tests. NaCl and KCl would both promote corrosion of metallic components and solutions of them used in a water mist fire suppression system would require clean up after use on a ship. The additives containing Cl could produce hydrogen chloride (HCl) and this would have an effect on materials and re-entry times and/or procedures for the space in which they were used.

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The use of both fixed and portable water mist systems for fire suppression on naval vessels continues to increase. There are several reasons for this. Water mist produces no acid gases and therefore can be discharged in a space where persons are present. It consists of small water droplets (average mean diameter of 90% of the droplets less than 300μm) that rapidly reduce the temperature in a space. The effectiveness of water mist in cooling a space reduces the volume of water necessary to extinguish or suppress a fire. This lessens both the chance of flooding and costs associated with cleanup arising from water damage.

In this report the use and efficacy of additives in water mist systems is reviewed. In most instances, additives have been investigated to determine if they will improve the efficacy of a water mist fire suppression system. Additives that have been investigated include film forming additives for Class B fires (generally fluorinated surfactants), alkali metals salts, transition metal chlorides, sulphates, phosphates and organic compounds such as sucrose and urea. In other instances, the additives were required to depress of the freezing point of the water used in the suppression systems. These suppression systems were proposed for use in conditions where the system might be exposed to temperatures below the freezing point of pure water. The additives included compounds such as potassium acetate and propylene glycol. The subsequent testing studied the effect of the additives on the water mist systems efficacy in suppressing a fire. Where information is available, the toxicity and other concerns associated with the use of additives are discussed.

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water mist; fire suppression; additives

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